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"Total Internal Reflection Second Harmonic Generation from the Interface Between
Two Immiscible Electrolyte Solutions"

by

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Total Internal Reflection Second Harmonic Generation from the Interface between Two Immiscible Electrolyte Solutions

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The nature of the electrochemical interface between two immiscible electrolyte solutions (ITIES) or liquid/liquid interfaces has been studied extensively due to the central role these systems play in chemistry and biology. The transport of molecular and ionic species across a liquid/liquid phase boundary is dependent upon the structure of the interfacial region and the electrostatic and intermolecular forces therein. Although numerous electrochemical studies of the ITIES double layer have appeared in the past few decades, an microscopic level understanding of the structure and order of both solute and solvent molecules at the interface remains elusive. Spectroscopic investigations of the interfacial structure or absorption of solvent or solute molecules at the interface has never been made due to experimental difficulties. There have been a number of spectroscopic investigations undertaken in order to ascertain the structure of these complex interfaces by monitoring the spectroscopic behavior of molecular surfactants adsorbed at the interface [1-3]. These studies have been very insightful but do not directly probe the properties of the native interface in the absence of the surfactant probe molecule.

In the studies to be described, optical second harmonic generation (SHG) is used to study the electrolytic water/1,2-dichloroethane (water/DCE) interface. SHG has been previously shown to be a very versatile tool for studying a variety of interfacial regions [4-6]. The SH response has been examined as a function of the applied potential and compared with more conventional electrochemical measurements. Previously such SH experiments have been difficult if not impossible to perform by SHG due to low signal levels. Success in performing the studies described herein has come from using a unique total internal reflection (TIR) geometry to enhance the interfacial SH response [7,8]. With this geometry, a 10-100 fold increase in SHG is achievable as the incident angle approaches the critical angle. Because of this enhanced sensitivity, one can measure for the first time the molecular properties of the DCE/water interface both in the presence and absence of electrolytes such as tetrabutylammonium tetraphenylborate (TBATPB) and LiCl. The studies to be described provide direct measurement of the potential induced adsorption of the TPB ion at this interface [9].

The measurements were performed in a cylindrical quartz cell which houses the reference and counter electrodes. The optical experiments were performed with the 532nm SH output of a Quanta-Ray DCR11 Nd:YAG laser. Pulses of 10ns duration and 2-5mJ at a repetition rate of 15 Hz were employed. The 532nm incident beam was collimated to a diameter of 0.25-0.5 mm and directed onto the interface from the 1,2-dichloroethane side of the interface and at the critical angle. The transmitted SH response at 266nm was passed through a series of absorptive and interference filters to remove any residual 532nm light. The generated SH light was polarization selected and detected with a PMT. The electrochemical and SH measurements were performed with 1.0 mM aqueous solutions of LiCl and TBACl. TBATPB (1.0 mM) was used as the supporting electrolyte in the DCE. The electrochemical measurements were performed with a four electrode potentiostat and waveform programmer. Platinum wire coils were used as counter electrodes in the aqueous and organic phases and placed directly above and below the interface. Ag/AgCl reference electrodes were used for both the aqueous and organic phases.

An example of the potential dependence in the SH response for the ITIES composed of 1.0 mM LiCl, aqueous and 1.0 mM TBATPB in DCE is shown in Figure 1. The corresponding cyclic voltammogram (CV) is displayed in Figure 2. Both sets of data were taken with potential limits of 100 mV to 520 mV and a scan rate of 5mV/sec. There is a potential window of 200mV from 0.200-0.400V under which the interface is ideally polarizable as seen by the negligible current flow in this region. Outside of this potential region, a large current is measured for potentials greater than 400mV and less than 100mV. Using the conventions previously established, the transfer of a positive charge from the aqueous to the organic phase is taken as the positive direction of

the current flow. The four curves displayed in Figure 1 are for the various polarization combinations, *P*-input and *P*-output polarization, *Mixed*(*S* and *P*)-input and *P*-output, *S*-input and *P*-output, and *Mixed*-input and *S*-output.

The observed SH signal potential dependence is attributed to a resonant SH effect. A resonant SH effect occurs when either the fundamental, here at 532nm, or the SH at 266nm are resonant with an optical transition in the material. The spectrum for the 0.1mM TBATPB in acetonitrile shows an absorption at 266nm resulting from a $\pi \rightarrow \pi^*$ transition of the phenyl rings in the TPB moiety. The observed SH intensity is then dependent upon the square of the surface concentration (*N*) and directly proportional to the extinction coefficient (ϵ). The conclusion that the potential dependent SH response is arising from the TPB ion at the interface can also be substantiated by the cyclic voltammogram. By examining the standard Gibbs energies of ion transfer across the water/DCE interface, the ions responsible for current flow in the CV of Figure 2 can be determined. The standard Gibbs energies for transport of an ion from the organic (o) to the aqueous (w) phases are 35.1kJ/mol and 21.8kJ/mol for TPB⁻ and TBA⁺ respectively. The corresponding values for Cl⁻ and Li⁺ are -46.4 kJ/mol and -54.0kJ/mol.[10,11] The value for Li⁺ was inferred from data on the water/nitrobenzene interface. From these values, the positive current in the CV (Figure 2) at potentials greater than 400mV is mainly due to the transfer of TPB⁻ ion and the negative current at potentials less than 100mV is due to that of TBA⁺ from the organic to the aqueous phase. The current due to the transport of Cl⁻ and Li⁺ is considered to be minimal from the comparison of the standard Gibbs energies of ion transport. From this analysis the observed increase in the SH response (Figure 1) at positive potentials correlates with the positive current flow in the CV of Figure 2 which is attributed to the transfer of TPB⁻.

As shown in Figure 1, all polarization combinations display the identical potential dependence taking into account the Fresnel factors for the incident and transmitted optical fields. This and other observations to be discussed suggest that the third order dc field $\chi^{(3)}$ contribution to the SH response is negligible. If the dc field strength was stronger, one would expect a much larger coupling to $\chi^{(3)}$ giving rise to different potential dependencies for the various polarization combinations. This is indeed true for higher electrolyte concentrations where the magnitude of the dc field at the interface is considerably stronger.

The resonance enhanced SH response from the TPB⁻ ion provides a basis for the relative determination of the TPB⁻ ion concentration at the interface as a function of the applied potential. The square root of the SH signal intensity is proportional to the concentration of the TPB⁻ ion at the interface. In this way, the potential dependent SH data can be used to make an optical measurement of the interfacial concentration of the TPB⁻ ion as a function of the applied potential. How such results compare with measured surface excess of the tetraphenylborate determined from the electrocapillary and capacitance measurements will be discussed as well as the accuracy of various models previously employed to understand this very important ITIES system.

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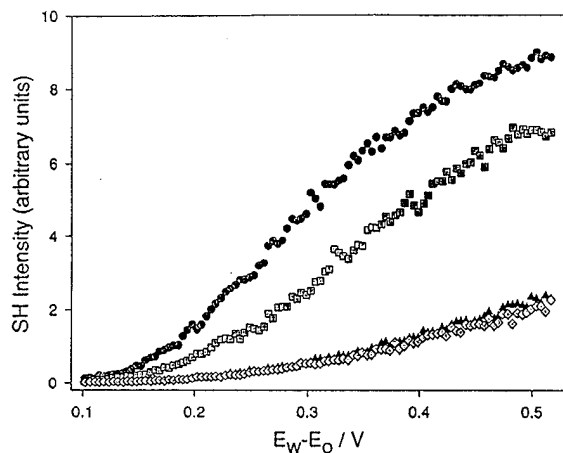


Figure 1: Potential dependent SH signal for the 1.0 mM LiCl (H_2O) / 1.0 mM TBATPB (DCE) interface. The following polarization combination are shown (&) P_{in} , P_{out} , (%) $Mixed_{in}$, P_{out} , (S) S_{in} , P_{out} , and (E) $Mixed_{in}$, S_{out} .

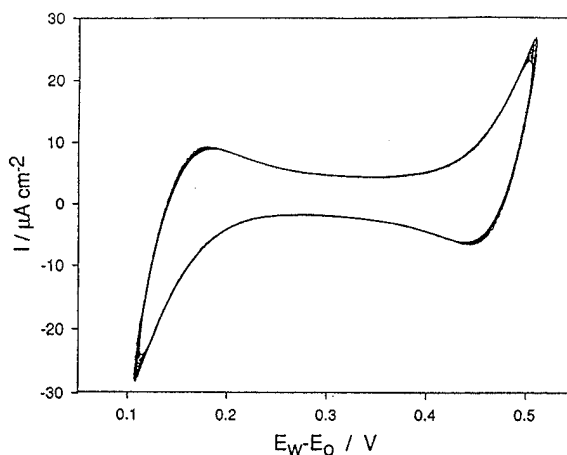


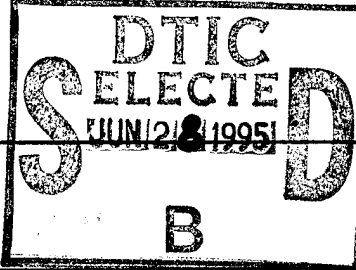
Figure 2: Cyclic voltammogram for the interface between an aqueous 1.0 mM LiCl and 1.0 mM TBATPB solution in DCE. The current was measured at a scan rate of 5 mV/sec as a function of the potential difference between the aqueous and organic phases, E_w-E_o .

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